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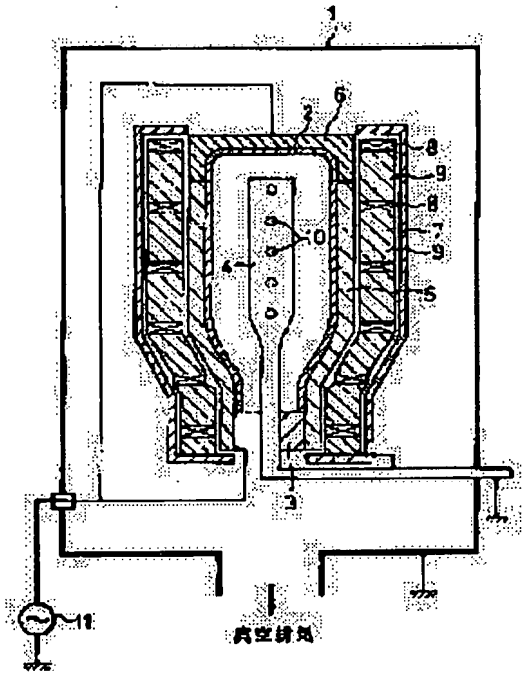
(54) FORMING METHOD OF DIAMONDLIKE CARBON FILM AND DEVICE FOR PRODUCING IT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a device capable of checking the transmission of a gas in a plastic vessel, without generating a damage to the inner wall face of the vessel even to the cleaning of the inner wall and capable of being repeatedly used.
SOLUTION: At the time of forming a diamondlike carbon film on the inner wall face of a plastic vessel 2, as a means of reinforcing plasma for promoting the cracking of a gaseous hydrocarbon raw material, a magnetic field is generated in the vicinity of the inner wall face of the plastic vessel, the number of times of the collision between electrons captured thereby and the gaseous hydrocarbon raw material is increased to accelerate the forming rate of the diamondlike carbon film, further, a negative self-bias voltage is generated on the inner wall face of the vessel and the cracked hydrocarbon ion seeds, carbon ions and hydrogen ions are made incident thereon to form the dense diamondlike carbon film.



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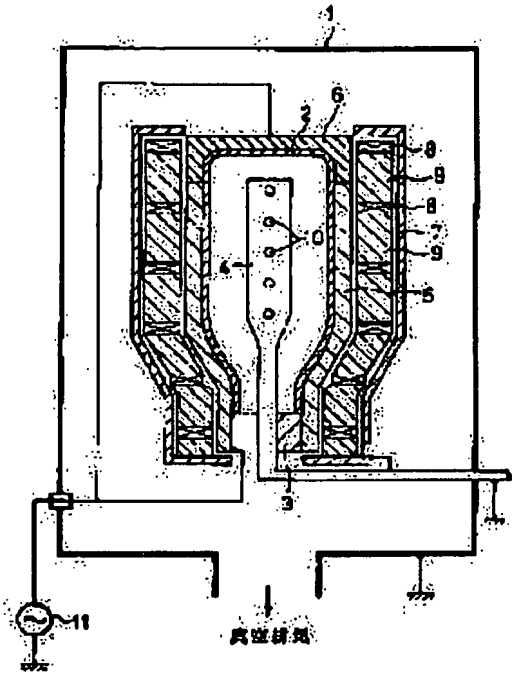

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CLAIMS

[Claim(s)]
[Claim 1] By the plasma-CVD method, it faces forming a diamond-like carbon film in a plastic envelope internal surface. A magnetic field is generated near the plastic envelope internal surface as an enhancement means of the plasma for promoting disassembly of coal-for-coke-making-ized hydrogen gas. Make [many] the count of a collision of the electron and coal-for-coke-making-ized hydrogen gas which were caught by that cause, and the generation rate of a diamond-like carbon film is enlarged. Moreover, the formation approach of the diamond-like carbon film characterized by carrying out incidence of the hydrocarbon ion kind, carbon ion, and hydrogen ion which this container internal surface was made to produce a negative auto-bias electrical potential difference, and were disassembled, and forming a precise diamond-like carbon film.
[Claim 2] The formation approach of the diamond-like carbon film according to claim 1 which is made to maintain magnetron discharge between the anode plates installed in the interior of this container, coal-for-coke-making-ized hydrogen gas is already, is made to disassemble it at a rate, is [a magnetic field is generated near / a plastic envelope internal surface / the above, and a RF, low frequency, or direct-current negative high tension is impressed to the cathode arranged so that this container may be wrapped, and] already in this container internal surface, and forms a precise diamond-like carbon film at a rate.
[Claim 3] The formation approach of the diamond-like carbon film according to claim 1 or 2 characterized by the above-mentioned raw material hydrogen gas being the simple substance gas or those mixed gas of the hydrocarbon chosen from saturated hydrocarbon, unsaturated hydrocarbon, and aromatic hydrocarbon.
[Claim 4] The formation approach of the diamond-like carbon film according to claim 1 to 3 characterized by introducing hydrogen, nitrogen, oxygen, the simple substance gas of argon gas, or those mixed gas into installation and coincidence of the above-mentioned coal-for-coke-making-ized hydrogen gas.
[Claim 5] The space which holds the plastic envelope processed in a vacuum tub, the cathode which has the inner surface configuration where the profile of the outer wall configuration of this plastic envelope was met, and is prepared on the outskirts of an outside of this plastic envelope, The internal anode plate which has the gas port prepared in this space surrounded in this cathode, The anode plate for discharge prevention arranged so that the insulating material prepared on the outskirts of a cathode outside other than the field in which two or more ring-like magnets and this magnet which are formed on the outskirts of an outside of this cathode, and this magnet are formed in contact with this magnet may be wrapped, and so that an edge may become close to this cathode, It comes to prepare the insulating material for supporting the this plastic envelope processed in a part of the regio-oralis head [at least]. And this cathode It consists of the first cathode parts and the dismountable second cathode parts which were fixed. After installing this plastic envelope on this insulating material for supporting this, it covers in the second cathode part and really becomes the cathode of an object. This insulating material for plastic envelope support The manufacturing installation of the diamond-like carbon film characterized by being prepared so that the inside of this plastic envelope can exhaust to a vacuum between this first cathode part and this internal anode plate.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach and manufacturing installation for forming the diamond-like carbon film which was excellent in the plastic envelope used for a plastic envelope by a bevel use and medical application especially by the plasma-CVD method about the approach and manufacturing installation for forming a diamond-like carbon film at gas barrier nature.
[0002]
[Description of the Prior Art] although the plastic envelope is used abundantly as a container in many fields, such as the food field and the drugs field, -- a plastics raw material -- it is used in the condition as it is.
[0003] For example, since it excels in transparency and gas barrier nature, the polyethylene terephthalate resin bottle (common-name PET bottle) is used abundantly as containers, such as soft drinks, such as alcoholic beverages, such as seasonings, such as soy sauce, and draft beer, and cola, and a detergent.
[0004] Moreover, since polyolefin resin is excellent in chemical resistance, it is used abundantly as a container raw material not only in package relation but in the various medical fields.
[0005] The plastics of much construction material are used not only in food and medical relation but in various fields above else.
[0006]
[Problem(s) to be Solved by the Invention] the conventional plastic envelope -- a raw material -- since it was used in the condition as it is and had the property that a gas like oxygen or a carbon dioxide will penetrate a vessel wall, and an organic compound will sorb a wall surface, there was a problem of contents deteriorating. For example, when a carbonated drink was saved at a plastic envelope, since the oxygen in atmospheric air penetrated a plastic envelope wall or the carbon dioxide gas contained in reverse at a carbonated drink penetrated out of a container, degradation was caused to quality, and the mothball was impossible. Moreover, although the plastic envelope used for remedies was excellent in chemical resistance, gas transmittance was large, and in order that this might also cause deterioration of drugs, there was a problem in respect of a mothball. Moreover, since hardness of plastics was small, breakage occurred in the container internal surface to washing of a container wall performed in order to use it repeatedly, and there was a problem in many activities.
[0007] This invention solves the problem which the above conventional things have, and it has hard and precise structure for a plastic envelope internal surface. And it is possible to cover with the diamond-like carbon (for it to also be hereafter called "DLC" (diamond like carbon)) film excellent also in chemical resistance, and to prevent transparency of gas. And it aims at offering the approach of forming a diamond-like carbon film in the plastic envelope internal surface which does not produce and cheat out of breakage to an internal surface to washing of a container wall and which is repeatedly used as an usable plastic envelope, and its manufacturing installation.
[0008]
[Means for Solving the Problem] The approach of forming the gas barrier film in the plastic envelope internal surface of this invention and its manufacturing installation are the approaches and equipment which form the hard and precise DLC film excellent also in chemical resistance in a container internal surface, in order to obtain the plastic envelope for a package which prevents transparency of gas and can be equal also to repeat washing.
[0009] In order to form the DLC film, the so-called plasma-CVD method the plasma decomposes and make

hydrocarbon gas deposit is used. However, the description of this invention is in generation of the plasma of high density, a ring-like magnet is used near the plastic envelope internal surface as an enhancement means for promoting decomposition of hydrocarbon gas, a magnetic field is generated, the count of a collision of the electron and coal-for-coke-making-ized hydrogen gas which were caught by that cause is made [many], and the generation rate of the DLC film is enlarged. RF potential, low frequency potential, or negative direct-current high tension is impressed to the cathode arranged on the outskirts of an outside of a container, and the internal electrode arranged inside a container is made into an anode plate (touch-down potential). Discharge takes place between cathode and an anode plate, an auto-bias electrical potential difference negative near the cathode with a container internal surface arises, the hydrocarbon ion kind, carbon ion, and hydrogen ion which were made by disassembly of a hydrocarbon carry out incidence to a container internal surface, and it is formed [the precise DLC film is very already and] with a generation rate.

[0010] As described above, any of RF potential, low frequency potential, or negative direct current voltage are sufficient as the potential impressed to cathode at the ring-like magnet made to generate a magnetic field using a permanent magnet or an electromagnet.

[0011] As coal-for-coke-making-ized hydrogen gas, there is especially no limit and it can use the hydrocarbon gas expressed with general formula:CmHn (however, m and n are integers.). Such hydrocarbon gas (CmHn) collides with an electron in the plasma. Cm'Hn'+ of an ionized state (However, m' and n' are integers.) Radical Cm"Hn" (m"and n" is an integer.) It is because change to carbon ion C+, C2+, C3+, etc., and CmHn collides with Cm'Hn'+, the hydrocarbon of a new ionization condition, the hydrocarbon of a radical, and carbon ion are generated further one after another, carbon accumulates by this and the DLC film is formed. As these coal-for-coke-making-ized hydrogen gas, the simple substance gas of aromatic hydrocarbon, such as unsaturated hydrocarbon, such as desirable saturated hydrocarbon, such as methane, ethane, a propane, butane, a pentane, a hexane, a heptane, an octane, a nonane, Deccan, an undecane, a dodecane, and an eicosane, or ethylene, acetylene, a propylene, and methylacetylene, or benzene, toluene, and naphthalene, or those mixed gas may be used.

[0012] Moreover, it is possible to introduce the simple substance gas or those mixed gas of hydrogen, nitrogen, oxygen, or argon gas into installation and coincidence of the above-mentioned coal-for-coke-making-ized hydrogen gas, to change the membraneous quality of the DLC film, to harden more or to increase translucency by installation of this gas.

[0013] In case the DLC film is formed, a ring-like magnet is arranged on the outside of the cathode which wraps a plastic envelope, and it is made for a magnetic field to occur near the plastic envelope wall with the equipment for enforcing the magnetron plasma-CVD method used according to this invention.

[0014] The space which holds the plastic envelope processed in a vacuum tub with this DLC film formation equipment, The cathode which has the inner surface configuration where the profile of the outer wall configuration of this plastic envelope was met, and is prepared on the outskirts of an outside of this plastic envelope, The internal anode plate which has the gas port prepared in this space surrounded in this cathode, The anode plate for discharge prevention arranged so that the insulating material prepared on the outskirts of a cathode outside other than the field in which two or more ring-like magnets and this magnet which are formed on the outskirts of an outside of this cathode, and this magnet are formed in contact with this magnet may be wrapped, and so that an edge may become close to this cathode, It comes to prepare the insulating material for supporting the this plastic envelope processed in a part of the regio-oralis head [at least]. And this cathode It is fixed and consists of a first cathode part and a dismountable second cathode part. After installing this plastic envelope on this insulating material for supporting this, it covers in the second cathode part and really becomes the cathode of an object. This insulating material for plastic envelope support It is prepared so that the inside of this plastic envelope can exhaust to a vacuum between this first cathode part and this internal anode plate.

[0015] Here, cathode peripheral faces other than the field in which the anode plate for discharge prevention is arranged so that a ring-like magnet may be wrapped, and this magnet is formed are filled with an insulating material, and discharge in the field in which this magnet has been arranged arises. Moreover, this insulating material for plastic envelope support should just be the thing of a gestalt from which the exhaust air of the inside of this plastic envelope to a vacuum is attained while being able to support this container, and contacting this first cathode part and this internal anode plate in part at least and being able to insulate.

[0016] If according to the equipment of this invention hydrocarbon gas is introduced and potential is impressed

to the first and the second cathode by the RF generator, the low frequency power source, or the direct-current negative supply from the blow-of-gas hole prepared in the internal anode plate after evacuation and in a plastic envelope, in a plastic envelope, magnetron discharge continues, and the DLC film [hard to a container wall and precise] excellent in chemical resistance will very already be, and will be formed with a generation rate.
[0017] According to this invention, the plastic envelope which consists of various plastics, such as a container made of polyethylene terephthalate resin and a container made of polyolefin resin, is contained in the plastic envelope which can be processed.
[0018] Moreover, a permanent magnet and an electromagnet can be used as a ring-like magnet.
[0019] Since according to the DLC film formation approach and manufacturing installation of this invention a magnetron plasma-CVD method can be used for a plastic envelope internal surface, the DLC film can be covered and transparency of the gas which lets a vessel wall pass is prevented, deterioration of the liquid in a container is lost and a mothball becomes possible. Moreover, since a container internal surface is covered with the hard film, this container is equal also to washing and a repeat activity is possible for it.
[0020] moreover, a generation of the DLC film [according to this invention] by magnetron plasma CVD sake -- the usual CVD -- comparing -- the generation rate of a coat -- markedly -- being alike -- there is a big advantage on the production to burn of becoming.
[0021]
[Example] Hereafter, the example of this invention is explained.
[0022] (Example 1) Drawing 1 shows the typical sectional view of the diamond-like carbon film formation equipment of this invention, and the plastic envelope, the electrode pattern, the magnet, etc. are formed in the vacuum tub 1. A plastic envelope 2 is placed so that it may support on the insulating material 3 for container support in a part of regio-oralis head of a container, and the inside of a container can exhaust it to a vacuum by preparing the part with which the regio oralis and an anode plate 4 (touch-down potential) are not in contact. It is fixed, and if it covers in the second cathode 6 after it puts in a plastic envelope 2 in the first cathode so that the internal anode plate 4 may be settled in a container from the direction of the regio oralis of a container, and the first cathode 5 places it on the insulating material 3 for container support, it is constituted so that the first and the second cathode may really turn into cathode of an object. The internal surface to which the configuration of cathode 5 and 6 meets the external wall surface of the plastic envelope at least met the profile of a plastic envelope outer wall configuration. Moreover, the circumference of an outside of cathode 5 and 6 other than the field in which an anode plate 7 is arranged so that two or more ring-like magnets 8 formed on the outskirts of an outside of cathode 5 and 6 may be wrapped, and it is made for the edge to become close to cathode 5 and 6, and the magnet 8 is formed is filled with an insulating material 9, and it is made to have not generated discharge in the field in which the magnet 8 has been arranged.
[0023] The DLC film was made to form using the above-mentioned equipment. First, after exhausting the vacuum tub 1 to a 10-3Pa grade, acetylene gas was introduced from the material gas blowout hole 10, and it was made the pressure of 26Pa. Then, impressed the high frequency potential of 13.56MHz to cathode 5 and 6 by output 500W from RF generator 11, magnetron discharge was made to cause, and the DLC film which was already in the internal surface of a plastic envelope 2, and was excellent in chemical resistance hard at a rate and precise was made to generate. The used plastic envelope is a polyethylene terephthalate resin bottle. The DLC film with a thickness of about 700nm was obtained by the membrane formation for 30 seconds (membrane formation rate 23.3 nm/s). Moreover, when based on the usual CVD performed by removing a magnet 8 from the above-mentioned equipment, the DLC film with a thickness of about 140nm was generated by the membrane formation for 30 seconds by the same actuation as the above (membrane formation rate 4.66 nm/s). That is, the generation rate was able to be increased about 5 times by using a magnetron method.
[0024] (Example 2) Although the same approach as an example 1 was repeated, benzene was used instead of acetylene as material gas. After exhausting the vacuum tub 1 to a 10-3Pa grade, introduced benzene gas from the blow-of-gas hole 10, impressed RF potential, magnetron discharge was made to cause, and the DLC film was generated. The thickness of the DLC film generated to the container wall by the membrane formation for [benzene gas pressure / of 26Pa / and high-frequency power 500] W or 20 seconds was about 1400nm (membrane formation rate 70.0 nm/s). Moreover, when based on the usual CVD which removed the magnet, thickness was about 260nm (13.0 nm/s). Thus, also when benzene gas was used, the membrane formation rate by magnetron plasma CVD was about 5 times the usual CVD.

[0025] (Example 3) The DLC film was generated on the same membrane formation conditions as an example 1 using the polyolefin resin bottle. By the magnetron method, about 680nm DLC film was formed of the membrane formation for 30 seconds (membrane formation rate 22.6 nm/s). On the other hand, where a magnet is removed, about 130nm DLC film was obtained by the membrane formation for 30 seconds (4.33 nm/s). This result is almost the same as the example 1 in the case of a polyethylene terephthalate resin bottle, and it has checked not being based on the construction material of a bottle.
[0026] When the difference in material gas was compared from examples 1 and 2, the generation rate of the DLC film was a big value of about 3 times in case the generation rate in the case of benzene is acetylene also in any of magnetron plasma CVD and the usual CVD.
[0027] Moreover it is usable also to the various chemicals which were excellent in gas barrier nature by being hard to a plastic envelope internal surface, and being precise, and covering the DLC film excellent also in chemical resistance, it can consider as an usable container repeatedly. By using a magnetron plasma-CVD method as a method of generating the DLC film, a generation rate can very already be and can consider as the good manufacture approach of productive efficiency.
[0028] In addition, although acetylene and benzene were used for material gas in the above-mentioned example instead, even if it uses methane, ethane, a propane, butane, a pentane, a hexane, a heptane, an octane, a nonane, Deccan, an undecane, a dodecane, saturated hydrocarbon like an eicosane or ethylene, a propylene, unsaturated hydrocarbon like MECHIRE acetylene or toluene, the simple substance gas of aromatic hydrocarbon like naphthalene, or those mixed gas, the same result as the case of the above-mentioned example is obtained. Moreover, even if it introduces the simple substance gas or those mixed gas of hydrogen, nitrogen, oxygen, or argon gas into installation and coincidence of the above-mentioned coal-for-coke-making-ized hydrogen gas, the same result as the case of the above-mentioned example is obtained.
[0029] Although the RF potential of 13.56MHz was impressed to cathode and discharge was made to cause in the above-mentioned example, whether it impresses other low frequency or RF potentials of a frequency or impresses negative direct-current high tension, the same result as the case of the above-mentioned example is obtained.
[0030] Furthermore, although the bottle which consists of polyethylene terephthalate resin and polyolefin resin as a plastic envelope was used in the above-mentioned example, even if it uses the plastic envelope which consists of various plastics, such as acrylic resin, polycarbonate resin, and polyamide resin, instead of them, the same result as the case of the above-mentioned example is obtained.
[0031] Although the ring-like permanent magnet was used in the above-mentioned example, an electromagnet may be used instead of it.
[0032]
[Effect of the Invention] Since it is characterized by making a plastic envelope wall generate a magnetic field to a discharge field in the plasma-CVD method which forms the DLC film, and making magnetron discharge maintain by that cause according to the diamond-like carbon film formation approach and manufacturing installation of this invention, the plasma is reinforced, and decomposition of the hydrocarbon gas which is a raw material is performed efficiently, therefore the generation rate of the DLC film becomes very large. In order that a hydrocarbon ion kind, carbon ion, and a hydrogen ion may carry out incidence to a plastic envelope wall at high speed, the precise DLC film is formed. Thereby, a plastic envelope does so effectiveness, such as becoming the thing excellent in gas barrier nature and chemical resistance.

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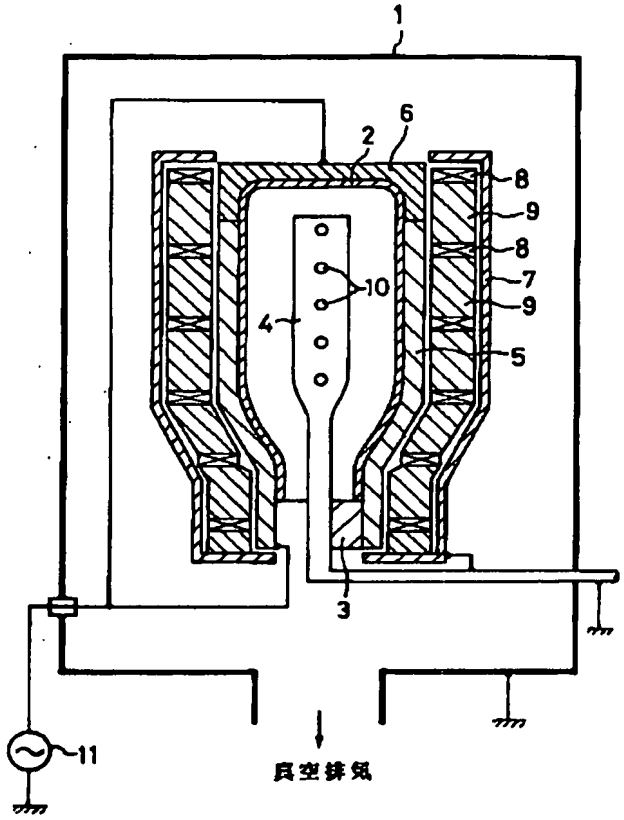
DRAWINGS

[Drawing 1]



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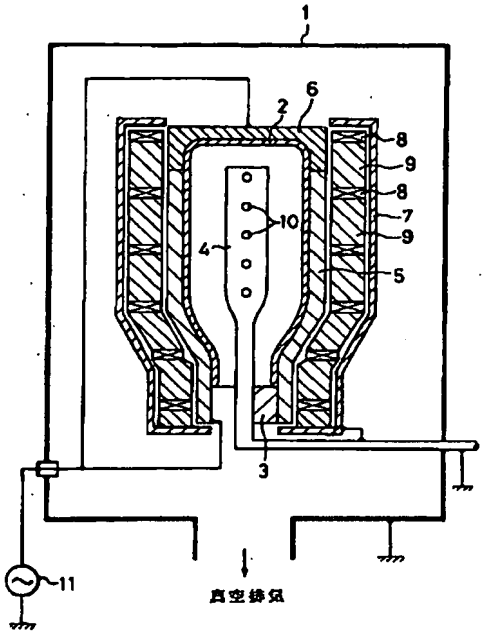
最終頁に続く

(54)【発明の名称】　ダイヤモンド状炭素膜形成方法及び製造装置

(57)【要約】

【課題】　プラスチック容器において、ガスの透過を阻止することが可能で、容器内壁の洗浄に対しても内壁面に損傷を生じせしめることのない、また、繰り返し使用可能なもの。

【解決手段】　プラスチック容器内壁面にダイヤモンド状炭素膜を形成するに際し、原料炭化水素ガスの分解を促進するためのプラズマの増強手段としてプラスチック容器内壁面近傍に磁場を発生させ、それにより捕捉された電子と原料炭化水素ガスとの衝突回数を多くしてダイヤモンド状炭素膜の生成速度を大きくし、また、その容器内壁面には負の自己バイアス電圧を生じさせて分解した炭化水素イオン種や炭素イオン及び水素イオンを入射させて緻密なダイヤモンド状炭素膜を形成する。



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【特許請求の範囲】

【請求項１】　プラズマＣＶＤ法により、プラスチック容器内壁面にダイヤモンド状炭素膜を形成するに際し、原料炭化水素ガスの分解を促進するためのプラズマの増強手段としてプラスチック容器内壁面近傍に磁場を発生させ、それにより捕捉された電子と原料炭化水素ガスとの衝突回数を多くしてダイヤモンド状炭素膜の生成速度を大きくし、また、該容器内壁面には負の自己バイアス電圧を生じさせて分解した炭化水素イオン種や炭素イオン及び水素イオンを入射させて緻密なダイヤモンド状炭素膜を形成することを特徴とするダイヤモンド状炭素膜の形成方法。

【請求項２】　上記プラスチック容器内壁面近傍に磁場を発生させ、該容器を包むように配置された陰極に高周波、もしくは低周波、もしくは直流負の高電圧を印加して、該容器内部に設置された陽極との間にマグネトロン放電を持続させ、原料炭化水素ガスをはやい速度で分解させて該容器内壁面にはやい速度で緻密なダイヤモンド状炭素膜を形成する請求項１記載のダイヤモンド状炭素膜の形成方法。

【請求項３】　上記原料水素ガスが、飽和炭化水素、不飽和炭化水素及び芳香族炭化水素から選ばれる炭化水素の単体ガス又はそれらの混合ガスであることを特徴とする請求項１又は２記載のダイヤモンド状炭素膜の形成方法。

【請求項４】　上記原料炭化水素ガスの導入と同時に、水素、窒素、酸素もしくはアルゴンガスの単体ガス、又はそれらの混合ガスを導入することを特徴とする請求項１～３のいずれかに記載のダイヤモンド状炭素膜の形成方法。

【請求項５】　真空槽内に、処理されるプラスチック容器を収容する空間、該プラスチック容器の外壁形状の輪郭に沿った内面形状を有しかつ該プラスチック容器の外側周辺に設けられる陰極、該陰極で囲まれた該空間内に設けられるガス噴出口を有する内部陽極、該陰極の外側周辺に設けられる複数のリング状磁石、該磁石と該磁石が設けられる領域以外の陰極外側周辺に該磁石に接して設けられる絶縁物とを包むようにかつ端部が該陰極に近くなるように配置される放電防止用陽極、及び該処理されるプラスチック容器をその口部先端の少なくとも一部で支持するための絶縁物を設けてなり、該陰極は、固定された第一陰極部分及び取り外し可能の第二陰極部分で構成され、該プラスチック容器をこれを支持するための該絶縁物の上に設置した後に、第二陰極部分で蓋をして一体物の陰極になるようになっており、該プラスチック容器支持用絶縁物は、該第一陰極部分と該内部陽極との間に該プラスチック容器内が真空に排気可能であるように設けられていることを特徴とするダイヤモンド状炭素膜の製造装置。

【発明の詳細な説明】

2

【０００１】

【発明の属する技術分野】本発明は、プラスチック容器にダイヤモンド状炭素膜を形成するための方法及び製造装置に関し、特にプラズマＣＶＤ法により飲料用や医療用に使用されるプラスチック容器にガスバリヤー性に優れたダイヤモンド状炭素膜を形成するための方法及び製造装置に関するものである。

【０００２】

【従来の技術】プラスチック容器は食品分野や医薬品分野等の多数の分野で包装容器として多用されているが、プラスチック素材そのままの状態で用いられている。

【０００３】例えば、ポリエチレンテレフタレート樹脂ボトル（通称ペットボトル）は透明性、ガスバリヤー性に優れているため、しょう油等の調味料、生ビール等のアルコール飲料、コーラ等の清涼飲料、洗剤等の包装容器として多用されている。

【０００４】また、ポリオレフィン樹脂は、耐薬品性に優れているため、包装関連のみならず、種々の医療分野で容器素材として多用されている。

【０００５】以上のほかに、数多くの材質のプラスチックスが、食品、医療関連のみならず、いろいろな分野で利用されている。

【０００６】

【発明が解決しようとする課題】従来のプラスチック容器は素材そのままの状態で使用されているので、容器壁を酸素や二酸化炭素のような気体が透過したり、また、壁面に有機化合物が収着してしまうという特性を有するため、内容物が変質するなどの問題があった。例えば、炭酸飲料をプラスチック容器に保存した場合、大気中の酸素がプラスチック容器壁を透過したり、あるいは逆に炭酸飲料に含まれる炭酸ガスが容器外に透過するため品質に劣化をきたし、長期保存が不可能であった。また、医薬用に使用されるプラスチック容器は耐薬品性には優れているものの、ガス透過度が大きく、これもまた医薬品の変質を起すため長期保存の点で問題があった。また、プラスチックは硬さが小さいため、繰り返し使用するために行われる容器内壁の洗浄に対して容器内壁面に損傷が発生し、多数回の使用には問題があった。

【０００７】本発明は、上記のような従来のもののもつ問題を解決するもので、プラスチック容器内壁面を硬くて緻密な構造を有し、かつ耐薬品性にも優れているダイヤモンド状炭素（以下、"DLC"(diamond like carbon)とも称す）膜で被覆して、ガスの透過を阻止することが可能で、かつ容器内壁の洗浄に対しても内壁面に損傷を生じさせしめることのない、繰り返し使用可能なプラスチック容器とする、プラスチック容器内壁面にダイヤモンド状炭素膜を形成する方法及びその製造装置を提供することを目的としている。

【０００８】

【課題を解決するための手段】本発明のプラスチック容

器内壁面にガスバリヤー膜を形成する方法及びその製造装置は、ガスの透過を阻止し、繰り返し洗浄にも耐え得る、包装用プラスチック容器を得るために、容器内壁面に硬くて緻密な、耐薬品性にも優れているＤＬＣ膜を形成する方法及び装置である。

【０００９】ＤＬＣ膜を形成するには、炭化水素ガスをプラズマにより分解して堆積させる、いわゆるプラズマＣＶＤ法を用いる。ただし、本発明の特徴は高密度のプラズマの生成にあり、炭化水素ガスの分解を促進するための増強手段としてプラスチック容器内壁面近傍にリング状磁石を用いて磁場を発生させ、それにより捕捉された電子と原料炭化水素ガスとの衝突回数を多くしてＤＬＣ膜の生成速度を大きくするものである。容器の外側周辺に配置した陰極に高周波電位、低周波電位、あるいは負の直流高電圧を印加し、容器の内側に配置した内部電極は陽極（接地電位）にする。陰極と陽極との間に放電が起り、容器内壁面で陰極近傍には負の自己バイアス電圧が生じて、炭化水素の分解によりできた炭化水素イオン種や炭素イオン及び水素イオンが容器内壁面に入射して緻密なＤＬＣ膜が非常にはやい生成速度で形成される。

【００１０】磁場を発生させるリング状磁石には永久磁石又は電磁石を用い、陰極に印加する電位は、上記したように、高周波電位、低周波電位、又は負の直流電圧のいずれでもよい。

【００１１】原料炭化水素ガスとしては特に制限はなく、一般式：ＣｍＨｎ（ただし、m及びnは整数である。）で表される炭化水素ガスが使用できる。このような炭化水素ガス（ＣｍＨｎ）は、プラズマ中で電子と衝突してイオン化状態のＣｍ'Ｈｎ''（ただし、m'及びn'は整数である。）やラジカルＣｍ''Ｈｎ''（ｍ''及びｎ''は整数である。）、炭素イオンC'、C''、C''などに変化し、さらにCmHnはCm'Hn''と衝突して次々に新しいイオン化状態の炭化水素やラジカルの炭化水素及び炭素イオンが発生し、これにより炭素が堆積してＤＬＣ膜を形成するからである。これらの原料炭化水素ガスとしては、好ましくは、メタン、エタン、プロパン、ブタン、ペンタン、ヘキサン、ヘプタン、オクタン、ノナン、デカン、ウンデカン、ドデカン、エイコサンなどのような飽和炭化水素、もしくはエチレン、アセチレン、プロピレン、メチルアセチレンなどのような不飽和炭化水素、もしくはベンゼン、トルエン、ナフタレンなどのような芳香族炭化水素の単体ガス、又はそれらの混合ガスが使用され得る。

【００１２】また、上記原料炭化水素ガスの導入と同時に水素、窒素、酸素もしくはアルゴンガスの単体ガス又はそれらの混合ガスを導入してもよく、このガスの導入により、ＤＬＣ膜の膜質を変え、より硬くしたり、あるいは透光性を増したりすることが可能である。

【００１３】本発明に従って用いるマグネトロンプラズマＣＶＤ法を実施するための装置では、ＤＬＣ膜を形成する際、プラスチック容器を包む陰極の外側にリング状磁石を配置し、磁場がプラスチック容器内壁近傍に発生するようにする。

【００１４】かかるＤＬＣ膜形成装置では、真空槽内に、処理されるプラスチック容器を収容する空間、該プラスチック容器の外壁形状の輪郭に沿った内面形状を有しかつ該プラスチック容器の外側周辺に設けられる陰極、該陰極で囲まれた該空間内に設けられるガス噴出口を有する内部陽極、該陰極の外側周辺に設けられる複数のリング状磁石、該磁石と該磁石が設けられる領域以外の陰極外側周辺に該磁石に接して設けられる絶縁物とを包むようにかつ端部が該陰極に近くなるように配置される放電防止用陽極、及び該処理されるプラスチック容器をその口部先端の少なくとも一部で支持するための絶縁物を設けてなり、該陰極は、固定され第一陰極部分及び取り外し可能の第二陰極部分で構成され、該プラスチック容器をこれを支持するための該絶縁物の上に設置した後に、第二陰極部分で蓋をして一体物の陰極になるようになっており、該プラスチック容器支持用絶縁物は、該第一陰極部分と該内部陽極との間に該プラスチック容器内が真空に排気可能であるように設けられている。

【００１５】ここで、リング状磁石を包むように放電防止用陽極を配置し、かつ、該磁石が設けられている領域以外の陰極外周面を絶縁物で満して、該磁石が配置された領域での放電が生じないようになっている。また、該プラスチック容器支持用絶縁物は、該容器を支持することができ、かつ、該第一陰極部分と該内部陽極とに少なくとも一部接触して、絶縁できると共に、該プラスチック容器内が真空に排気可能となるような形態のものであればよい。

【００１６】本発明の装置によれば、真空排気後、プラスチック容器内の内部陽極に設けられたガス噴出孔より炭化水素ガスを導入し、第一及び第二陰極に高周波電源、又は低周波電源、又は直流負電源により電位を印加すると、プラスチック容器内にマグネトロン放電が持続し、容器内壁に硬くて緻密な、耐薬品性に優れたＤＬＣ膜が非常にはやい生成速度で形成される。

【００１７】本発明に従って処理可能のプラスチック容器には、ポリエチレンテレフタレート樹脂製容器、ポリオレフィン樹脂製容器等のいろいろなプラスチックからなるプラスチック容器が含まれる。

【００１８】また、リング状磁石としては、永久磁石や、電磁石を用いることができる。

【００１９】本発明のＤＬＣ膜形成方法及び製造装置によれば、プラスチック容器内壁面にマグネトロンプラズマＣＶＤ法を用いてＤＬＣ膜を被覆することができるので、容器壁を通してのガスの透過が阻止されるため、容器内の液体の変質がなくなり、長期保存が可能となる。また、容器内壁面は硬質膜で被覆されるため、該容器は

洗浄にも耐え、繰り返し使用が可能である。

【００２０】また、本発明によれば、マグネトロンプラズマＣＶＤによるＤＬＣ膜の生成のため、通常のＣＶＤに比べて被覆の生成速度が格段にはやくなるという生産上の大きな利点がある。

【００２１】

【実施例】以下、本発明の実施例を説明する。

【００２２】（実施例１）図１は、本発明のダイヤモンド状炭素膜形成装置の模式的断面図を示すものであり、真空槽１内にプラスチック容器、放電用電極、磁石等が設けられている。プラスチック容器２は容器支持用絶縁物３の上に容器の口部先端の一部で支えられるように置かれ、口部と陽極４（接地電位）とが接していない部分を設けることにより容器内が真空に排気可能となっている。第一陰極５は固定されており、プラスチック容器２を容器の口部の方から内部陽極４が容器内に収まるように第一陰極内に入れて容器支持用絶縁物３の上に置いた後、第二陰極６で蓋をすると、第一及び第二陰極が一体物の陰極になるように構成されている。陰極５及び６の形状は、少なくともそのプラスチック容器の外壁面に対面する内壁面がプラスチック容器外壁形状の輪郭に沿ったようになっている。また、陽極７は陰極５及び６の外側周辺に設けられた複数のリング状磁石８を包むように配置され、その端部が陰極５及び６に近くなるようにされ、かつ、磁石８が設けられている領域以外の陰極５及び６の外側周辺を絶縁物９で満して、磁石８が配置された領域での放電が発生しないようにしてある。

【００２３】上記装置を用いてＤＬＣ膜を形成せしめた。まず、真空槽１を10^{-3}Ｐａ程度に排気した後、原料ガス噴出孔１０からアセチレンガスを導入し、２６Ｐａの圧力にした。その後、陰極５及び６に高周波電源１１から１３．５６ＭＨｚの高周波電位を出力５００Ｗで印加してマグネトロン放電を起させ、プラスチック容器２の内壁面にはやい速度で硬くて緻密な、耐薬品性に優れたＤＬＣ膜を生成させた。用いたプラスチック容器はポリエチレンテレフタレート樹脂ボトルである。３０秒間の成膜により厚さ約７００ｎｍのＤＬＣ膜が得られた（成膜速度２３．３ｎｍ／ｓ）。また、上記装置から磁石８を取り除いて行った通常のＣＶＤによる場合には、前記と同様の操作により、３０秒間の成膜で厚さ約１４０ｎｍのＤＬＣ膜が生成された（成膜速度４．６６ｎｍ／ｓ）。すなわち、マグネトロン方式を用いることにより生成速度を約５倍にすることができた。

【００２４】（実施例２）実施例１と同様の方法を繰り返したが、原料ガスとしてアセチレンの代りにベンゼンを用いた。真空槽１を10^{-3}Ｐａ程度に排気した後、ガス噴出孔１０からベンゼンガスを導入して高周波電位を印加し、マグネトロン放電を起させてＤＬＣ膜を生成した。ベンゼンガス圧力２６Ｐａ、高周波電力５００Ｗ、２０秒間の成膜で容器内壁に生成したＤＬＣ膜の厚さは約１４００ｎｍであった（成膜速度７０．０ｎｍ／ｓ）。また、磁石を取り除いた通常のＣＶＤによる場合には、膜厚は約２６０ｎｍであった（１３．０ｎｍ／ｓ）。この様にベンゼンガスを用いた場合もマグネトロンプラズマＣＶＤによる成膜速度は通常のＣＶＤの約５倍であった。

【００２５】（実施例３）ポリオレフィン樹脂ボトルを用いて実施例１と同一成膜条件でＤＬＣ膜の生成を行った。マグネトロン方式では３０秒間の成膜により約６８０ｎｍのＤＬＣ膜が形成された（成膜速度２２．６ｎｍ／ｓ）。一方、磁石を取り除いた状態では、３０秒間の成膜で約１３０ｎｍのＤＬＣ膜が得られた（４．３３ｎｍ／ｓ）。この結果は、ポリエチレンテレフタレート樹脂ボトルの場合の実施例１とほぼ同じであり、ボトルの材質によらないことが確認できた。

【００２６】実施例１及び２から、原料ガスの違いを比べてみると、ＤＬＣ膜の生成速度は、マグネトロンプラズマＣＶＤ及び通常のＣＶＤのいずれにおいても、ベンゼンの場合の生成速度がアセチレンの場合の約３倍という大きな値であった。

【００２７】プラスチック容器内壁面に硬くて、緻密な、かつ耐薬品性にも優れたＤＬＣ膜を被覆することにより、ガスバリヤー性に優れた、種々の薬品にも使用可能な、また、繰り返し使用可能な容器とすることができる。ＤＬＣ膜の生成法としてマグネトロンプラズマＣＶＤ法を用いることにより生成速度が非常にはやい、生産効率のよい製造方法とすることができる。

【００２８】なお、上記実施例では原料ガスにはアセチレン及びベンゼンを用いたが、その代りにメタン、エタン、プロパン、ブタン、ペンタン、ヘキサン、ヘプタン、オクタン、ノナン、デカン、ウンデカン、ドデカン、エイコサンのような飽和炭化水素、もしくはエチレン、プロピレン、メチレアセチレンのような不飽和炭化水素、もしくはトルエン、ナフタレンのような芳香族炭化水素の単体ガス、又はそれらの混合ガスを用いても上記実施例の場合と同様な結果が得られる。また、上記原料炭化水素ガスの導入と同時に水素、窒素、酸素もしくはアルゴンガスの単体ガス又はそれらの混合ガスを導入しても、上記実施例の場合と同様な結果が得られる。

【００２９】上記実施例では陰極に１３．５６ＭＨｚの高周波電位を印加して放電を起させたが、他の周波数の低周波あるいは高周波電位を印加しても、又は負の直流高電圧を印加しても上記実施例の場合と同様な結果が得られる。

【００３０】さらに、上記実施例では、プラスチック容器としてポリエチレンテレフタレート樹脂及びポリオレフィン樹脂からなるボトルを用いたが、それらに代わりアクリル樹脂、ポリカーボネート樹脂、ポリアミド樹脂等のいろいろなプラスチックからなるプラスチック容器を用いても、上記実施例の場合と同様な結果が得られ

る。

【００３１】上記実施例ではリング状永久磁石を用いたが、それに代わり電磁石を用いてもよい。

【００３２】

【発明の効果】本発明のダイヤモンド状炭素膜形成方法及び製造装置によれば、プラスチック容器内壁にＤＬＣ膜を形成するプラズマＣＶＤ法において、放電領域に磁場を発生させ、それによりマグネトロン放電を持続させることを特徴としているので、プラズマは増強されて原料である炭化水素ガスの分解が効率よく行われ、従ってＤＬＣ膜の生成速度が非常に大きくなる。プラスチック容器内壁には炭化水素イオン種、炭素イオン、水素イオンが高速で入射するため緻密なＤＬＣ膜が形成される。＊これによりプラスチック容器はガスバリヤー性、耐薬品性に優れたものとなるなどの効果を奏する。

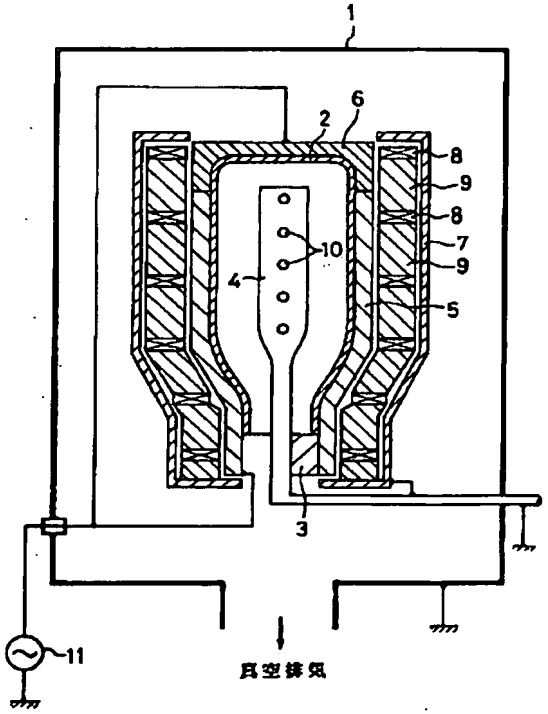
【図面の簡単な説明】

【図１】本発明の実施例におけるＤＬＣ膜の製造に使用する装置の模式的断面図である。

【符号の説明】

１　真空槽	２　プラスチック容器
３　容器支持用絶縁物	４　内部陽極
５　第一陰極	６　第二陰極
７　陽極	８　リング状磁石
９　絶縁物	１０　ガス噴出孔
１１　高周波電源	

【図１】



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